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(71)Applicant : FUJI PHOTO FILM CO LTD

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(72)Inventor : INOUE HIROSHI

YASUNAMI SHOICHIRO

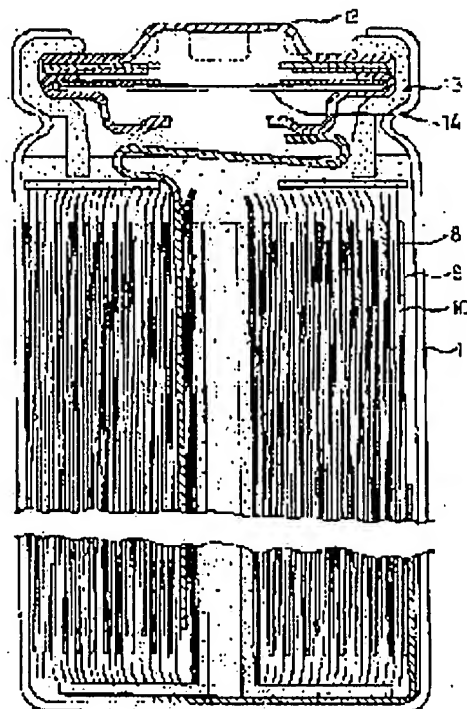
INOUE AKIYUKI

(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve productivity of a highly safe nonaqueous secondary battery provided with a high discharge voltage and an excellent charge-discharge cycle characteristic by forming a specific protecting layer on a negative electrode and/or a positive electrode.

SOLUTION: A nonaqueous secondary battery is constructed of a positive electrode and a negative electrode, which contain materials plastically storing/releasing lithium, a nonaqueous electrolyte containing lithium salt, and a separator, and in the negative electrode and/or the positive electrode, at least one protecting layer formed of solid particles and a water soluble polymer is formed. In the protecting layer, conductive particles may be contained in addition to the solid particles and the water soluble polymer. The thickness of the protecting layer is 1-40 μ m desirably. An inorganic chalcogenide particle is feasible for the solid particle contained in the protecting layer. A polyacrylic derivative or a cellulose derivative is feasible for the water soluble polymer. For the conductive particle, a carbonaceous compound, natural graphite, and vapor phase growth carbon are desirable in particular.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the nonaqueous rechargeable battery which raised productivity and which is excellent in a life and safety with high discharge potential.

[0002]

[Description of the Prior Art] The protective layer which becomes JP,61-7577,A from the matter having electronic conductivity and ion conductivity, such as a lithium, about the front face of a positive electrode is indicated, and it is indicated that the oxide of a tungsten, molybdenum, and vanadium is desirable as matter which has electronic-ion mixing conductivity. However, these compounds have come to show sufficient effectiveness of preventing an internal short circuit. Moreover, installing the poly membrane which penetrates this alkali-metal ion alternatively on a positive electrode and the negative-electrode (alkali-metal or alkali-metal alloy) side which counters is indicated by JP,4-28173,A. However, installation of these porous poly membranes has conceived the problem on which cell capacity is reduced sharply.

[0003]

[Problem(s) to be Solved by the Invention] Therefore, the technical problem of this invention is raising the productivity of the nonaqueous rechargeable battery in which had high discharge voltage and a good charge-and-discharge cycle property, and safety's was further excellent.

[0004]

[Means for Solving the Problem] In the positive electrode which contains reversibly the ingredient in which occlusion emission is possible for a lithium and a negative electrode, the nonaqueous electrolyte containing lithium salt, and the nonaqueous rechargeable battery that consists of a separator, this negative electrode and/or a positive electrode have at least one layer of protective layers, and the technical problem of this invention was attained by the nonaqueous rechargeable battery characterized by becoming if these protective layers are a solid particulate and a water-soluble polymer.

[0005]

[Embodiment of the Invention] The positive electrode and negative electrode with which this invention persons contain reversibly the ingredient in which occlusion emission is possible for a lithium, The place which considered wholeheartedly the bad cause of the manufacture yield of the nonaqueous electrolyte containing lithium salt, and the nonaqueous rechargeable battery which consists of a separator, The irregularity of the letter of a projection of an electrode surface, the blemish of the electrode surface produced from conveyance of an electrode to cell assembly in process, It turned out that contribution of the irregularity by partial omission etc. having become a cause and the internal short circuit having occurred by destroying a separator directly at the time of cell winding, or being connected with delicate sliding at the time of winding and the unevenness of a pressure, and destroying a separator is large. In order to prevent a section short circuit among these, it was effective in the electrode surface to prepare a protective layer, and while installation of a protective layer raised the manufacture yield, it turned out that safety is also raised. Furthermore, it turned out that the above can be attained, without

being accompanied by the fall of discharge capacity, especially the discharge capacity in a high current because a protective layer contains a water-soluble polymer excluding a resin binder.

[0006] Although the desirable mode of this invention is shown below, this invention is not limited to these.

(1) The nonaqueous rechargeable battery which this negative electrode and/or a positive electrode have at least one layer of protective layers, and is characterized by becoming if these protective layers are a solid particulate and a water-soluble polymer in the positive electrode which contains reversibly the ingredient in which occlusion emission is possible for a lithium and a negative electrode, the nonaqueous electrolyte containing lithium salt, and the nonaqueous rechargeable battery that consists of a separator.

(2) The nonaqueous rechargeable battery characterized by for this negative electrode and/or a positive electrode having at least one layer of protective layers, and this protective layer consisting of a solid particulate, a conductive particle, and a water-soluble polymer in the positive electrode which contains reversibly the ingredient in which occlusion emission is possible for a lithium and a negative electrode, the nonaqueous electrolyte containing lithium salt, and the nonaqueous rechargeable battery that consists of a separator.

(3) (1) to which thickness of this protective layer is characterized by 1-micrometer or more being 40 micrometers or less Or (2) Nonaqueous rechargeable battery of a publication.

(4) (3) characterized by forming this protective layer on a negative electrode Nonaqueous rechargeable battery of a publication.

(5) (3) characterized by forming this protective layer on a positive electrode Nonaqueous rechargeable battery of a publication.

(6) (3) characterized by forming this protective layer in both on a positive electrode and a negative electrode Nonaqueous rechargeable battery of a publication.

(7) (3) characterized by this protective layer containing a conductive particle on a negative electrode excluding a conductive particle on a positive electrode Nonaqueous rechargeable battery of a publication.

(8) (4) characterized by the solid particulate contained in this protective layer being an inorganic chalcogenide particle from -- (7) Nonaqueous rechargeable battery given in any 1 term.

(9) (8) characterized by this inorganic chalcogenide particle containing at least one sort of oxides of sodium, a potassium, magnesium, calcium, strontium, a zirconium, aluminum, and silicon Nonaqueous rechargeable battery of a publication.

(10) (9) characterized by the oxide of (9) being an alumina, a silicon dioxide, and a zirconia Nonaqueous rechargeable battery of a publication.

(11) (8) characterized by the water-soluble polymer contained in a protective layer being a polyacrylic acid derivative or a cellulosic from -- nonaqueous rechargeable battery given in any 1 term of (10). (12) A nonaqueous rechargeable battery given in (11) characterized by the conductive particle contained in a protective layer being a carbon material.

(13) A nonaqueous rechargeable battery given in (12) characterized by the negative-electrode ingredient in which occlusion emission is possible using a lithium as a metallic oxide reversibly.

(14) A nonaqueous rechargeable battery given in (13) characterized by being the multiple oxide with which this negative electrode contains tin.

(15) A nonaqueous rechargeable battery given in (14) characterized by the multiple oxide containing this tin being a multiple oxide of the following general formula (1).

SnM1 a Ot General formula (1)

The inside of a formula, and M1 Expressing aluminum, B, P, Si, the 1st group element of the periodic table, the 2nd group element, the 3rd group element, and two or more sorts of elements chosen from a halogen, a expresses or more 0.2 two or less number, and t expresses or more 1 six or less number.

(16) A nonaqueous rechargeable battery given in (15) characterized by the multiple oxide containing this tin being a multiple oxide of the following general formula (2).

SnM2 b M3 c Ot General formula (2)

The inside of a formula, and M2 They are at least two sorts of aluminum, B, P, and Si M3 Expressing at least one sort of the 1st group element of the periodic table, the 2nd group element, the 3rd group element, and a halogen, b is or more 0.2 two or less number, c is or more 0.01 one or less number, and $0.2 < b + c < 2$ and t express or more 1 six or less number.

(17) (1) characterized by connecting this negative electrode to a metal lithium electrically from -- nonaqueous rechargeable battery given in (16).

[0007] In this invention, a protective layer consists of at least one layer, and may be constituted by congener or two or more layers of a different kind. The thickness of a protective layer has 1 micrometers or more desirable 40 micrometers or less, and it is 2 micrometers or more 30 micrometers or less more preferably. Furthermore, as for the protective layer containing these particles, what does not form a coat new in dissolving below 300 degrees C is desirable. These protective layers may also be included in accordance with a solid particulate organic [conductive] or inorganic including an organic or inorganic solid particulate without conductivity. An inorganic solid particulate is more desirable among these particles.

[0008] As an inorganic substance particle, a metal, the carbide of a nonmetallic element, silicide, a nitride, a sulfide, and an oxide can be mentioned. In carbide, silicide, and a nitride, SiC, aluminum nitride (AlN), and BN and BP of insulation are chemically [highly and] stable, and are desirable, and especially SiC using especially BeO, Be, and BN as a sintering assistant is desirable. In chalcogenide, an oxide is desirable and the oxide which oxidizes or is hard to be returned is desirable. As these oxides, it is aluminum $2O_3$, As $4O_6$, B-2 O_3 , BaO, BeO and CaO, Li2 O, K2 O, Na2 O, In $2O_3$, MgO, Sb $2O_5$, SiO₂, SrO, and ZrO₂. It is raised. the inside of these -- aluminum $2O_3$, BaO, BeO and CaO, K2 O, Na2 O, MgO and SiO₂, SrO, and ZrO₂ It is especially desirable. These oxides may be independent or may be multiple oxides. As a compound desirable as a multiple oxide, a mullite (3aluminum $2O_3$ and 2SiO₂), a steatite (MgO-SiO₂), forsterite (2 MgO-SiO₂), cordierite (2MgO, 2aluminum $2O_3$, and 5SiO₂), etc. can be mentioned. As a conductive particle, an inorganic particle is desirable and the particle of a metal powder, inorganic chalcogenide, and a carbonaceous compound is mentioned. Especially, a carbonaceous compound, a natural graphite, and vapor growth carbon are desirable.

[0009] 0.1 micrometers or more 20 micrometers or less are especially used preferably by approaches, such as control of a generation condition, and grinding, by making these inorganic compound particles into 0.2-micrometer or more particle 15 micrometers or less.

[0010] the content of the particle used for this invention -- 1 - 80 g/m² -- it is 2 - 40 g/m² preferably. A protective layer is formed mainly from above-mentioned solid particulate and water-soluble polymer which do not have conductivity substantially, or the above-mentioned solid particulate which does not have conductivity substantially, a conductive solid particulate, and a water-soluble polymer. 96 or less % of the weight 40 % of the weight or more has a desirable particle to both AUW, and the ratio of a solid particulate and a water-soluble polymer has 92 or less more desirable % of the weight 50 % of the weight or more. As a water-soluble polymer, there are cellulose, such as a carboxymethyl cellulose and hydroxyethyl cellulose, a polyacrylic acid derivative, a polyvinyl alcohol derivative, a polyethylene oxide derivative, starch, etc., and a cellulosic and a polyacrylic acid derivative are desirable.

[0011] A protective layer may be painted on a positive electrode or a negative electrode, or may be painted on both positive electrode and negative electrode. Moreover, when a positive electrode and a negative electrode paint a mixture on the both sides of a charge collector and are formed in them, a protective layer may be a gestalt which may paint on the both sides and is painted only on one side. However, it needs to be painted on the positive electrode or the negative electrode which opposes through a separator. The painting method of a protective layer may be a coincidence spreading method which carries out sequential painting of the protective layer and which a method is sufficient as serially and paints a binder layer and a protective layer on coincidence, after painting the mixture which contains reversibly the ingredient in which occlusion emission is possible for a lithium on a charge collector.

[0012] forward and the negative electrode which are used for the nonaqueous rechargeable battery of this invention -- a positive electrode -- a mixture or a negative electrode -- a mixture can be painted on a charge collector and can be made. a positive electrode or a negative electrode -- everything but positive

active material or a negative-electrode ingredient can be looked like [a mixture], respectively, and can contain an electric conduction agent, a binder, a dispersant, a filler, an ion electric conduction agent, a pressure enhancement agent, and various additives in it, respectively.

[0013] As a negative-electrode ingredient used by this invention, what is necessary is just the compound which can carry out occlusion emission of the light metal ion. Although there are a light metal, a light metal alloy, a carbonaceous compound, an inorganic oxide, inorganic chalcogenide, a metal complex, and an organic high molecular compound in these, a carbonaceous compound, an inorganic oxide, and inorganic chalcogenide are desirable. Furthermore, these may combine and use. For example, the combination of a light metal, a carbonaceous compound and a light metal, an inorganic oxide and a light metal, a carbonaceous compound, and an inorganic oxide etc. is mentioned. Since these negative-electrode ingredients give the effectiveness of high capacity, high discharge potential, Takayasu all nature, and high cycle nature, they are desirable. As light metal ion, a lithium is desirable.

[0014] What is chosen from a natural graphite, an artificial graphite, vapor growth carbon, the carbon with which the organic substance was calcinated as a carbonaceous compound, and includes graphite structure is desirable. Moreover, a different-species compound, for example, B, P, N, S, and SiC, and B₄C may also be included in a carbonaceous compound zero to 10% of the weight besides carbon.

[0015] As an element with which ***** forms chalcogenide, the periodic table 13 to 15 groups' metal and metalloid element of ***** are desirable. As a transition-metals compound, independent, the multiple oxide, or chalcogenide of V, Ti, Fe, Mn, Co, nickel, Zn, W, and Mo is especially desirable. Furthermore, as a desirable compound, Lip Coq V1-q Or (it is $p=0.1-2.5$, $q=0-1$, and $z=1.3-4.5$ here) given in JP,6-44,972,A can be mentioned.

[0016] As a compound of metals other than transition metals, and semimetal, the 13th group of the periodic table - 15 group's element, independent or the oxide which consists of two or more sorts of those combination of Ga, Si, Sn, germanium, Pb, Sb, and Bi, and chalcogenide are chosen. For example, Ga₂O₃, SiO, GeO and GeO₂, SnO, and SnO₂, SnSiO₃, PbO, PbO₂, Pb₂O₃, and Pb₂O₄, Pb₃O₄, Sb₂O₃, Sb₂O₄, and Sb₂O₅, Bi₂O₃, Bi₂O₄, Bi₂O₅, SnSiO₃, GeS, GeS₂, SnS, SnS₂, PbS, PbS₂, Sb₂S₃, Sb₂S₅, and SnSiS₃ etc. -- it is desirable. moreover, these -- Li₂SnO, a multiple oxide 3, for example, Li₂GeO, with lithium oxide, 2 you may be.

[0017] As for the above-mentioned compound chalcogen compound and a multiple oxide, it is desirable that it is mainly amorphous at the time of cell inclusion. An amorphous substance is an object which has the broadcloth dispersion band which has top-most vertices from 20 degrees to 40 degrees with 2theta value with the X-ray diffraction method which is said here, and which used CuK alpha rays, and you may mainly have a crystalline diffraction line. the strongest reinforcement is 500 or less times of the diffraction line intensity of the top-most vertices of the broadcloth dispersion band looked at by 20 degrees or more 40 degrees or less with 2theta value among the crystalline diffraction lines preferably looked at by 40 degrees or more 70 degrees or less with 2theta value -- desirable -- further -- desirable -- 100 or less times -- it is -- especially -- desirable -- 5 or less times -- it is -- most -- desirable -- It is not having a crystalline diffraction line.

[0018] The above-mentioned compound chalcogen compound and a multiple oxide are the compound chalcogen compound of three or more sorts of elements in B, aluminum, Ga, In, Tl, Si, germanium, Sn, Pb, P, As, Sb, and Bi, and a multiple oxide, and are a multiple oxide more preferably. It is the multiple oxide which consists of three or more sorts of elements in B, aluminum, Si, germanium, Sn, and P preferably especially. Since amorphous structure is mainly embellished, these multiple oxides may also contain the periodic table's element or halogen of one to three groups.

[0019] In the above-mentioned negative-electrode ingredient, especially the amorphous multiple oxide that makes tin a subject is desirable, and it is expressed with the following general formula (1).

SnM1 a Ot General formula (1)

The inside of a formula, and M1 Expressing aluminum, B, P, Si, the 1st group element of the periodic table, the 2nd group element, the 3rd group element, and two or more sorts of elements chosen from a halogen, a expresses or more 0.2 two or less number, and t expresses or more 1 six or less number.

[0020] In a general formula (1), the compound of the following general formula (2) is still more

desirable.

SnM2 b Ot General formula (2)

The inside of a formula, and M2 Expressing aluminum, B, P, the 1st group element of the periodic table, the 2nd group element, the 3rd group element, and two or more sorts of elements chosen from a halogen, b expresses or more 0.2 two or less number, and t expresses or more 1 six or less number.

[0021] In a general formula (1), the compound of the following general formula (3) is still more desirable.

SnM3 c M4 d Ot General formula (3)

The inside of a formula, and M3 They are at least two sorts of aluminum, B, P, and Si M4 Expressing at least one sort of the 1st group element of the periodic table, the 2nd group element, the 3rd group element, and a halogen, c is or more 0.2 two or less number, d is or more 0.01 one or less number, and $0.2 < c + d < 2$ and t express or more 1 six or less number. M3 M4 It is an element for making the compound of a general formula (3) make it amorphous as a whole, and is M3. It is the element in which un-crystallizing is possible, and it is desirable to use combining two or more sorts of aluminum, B, P, and Si. M4 It is the element in which amorphous qualification is possible, and it is the 1st group element of the periodic table, the 2nd group element, the 3rd group element, and a halogen, and K, Na, Cs, Mg, calcium, Ba, Y, and F are desirable. b is or more 0.2 two or less number, c is or more 0.01 one or less number, and $0.2 < b + c < 2$ and t express or more 1 six or less number.

[0022] Although any approach of the calcinating method and a solution method can be used for the amorphous multiple oxide of this invention, its calcinating method is more desirable. After often mixing the oxide or compound of an element indicated by the general formula (1) by the calcinating method, it is desirable to calcinate and to obtain an amorphous multiple oxide.

[0023] As baking conditions, it is desirable that it is 5-degree-C [or more]/m programming rate of 200 degrees C or less as a programming rate, it is desirable as a burning temperature that it is [500 degrees-C or more] 1500 degrees C or less, and it is desirable that it is 100 or less hours as firing time for 1 hour or more. And it is desirable that it is below 2-degree-C[or more]/m 107 ** as a bottom temperature fall rate. The programming rate in this invention is the mean velocity of a temperature rise until it reaches "80% of burning temperature (degree-C display)" from "50% of burning temperature (degree-C display)", and the temperature fall rate in this invention is the mean velocity of a temperature reduction until it reaches "50% of burning temperature (degree-C display)" from "80% of burning temperature (degree-C display)." You may cool all over a firing furnace and a temperature fall is taken out outside a firing furnace again, for example, may be supplied underwater and may be cooled. moreover, gun given in 217 pages (Gihodo Shuppan 1987) of ceramic processing -- law -Hammer-Anvil -- law -slap -- law -- the - gas atomizing method, the plasma-spraying method, a centrifugal quenching method, and melt drag -- super-quenching methods, such as law, can also be used. Moreover, you may cool using the single roller method given in 172 pages (Maruzen 1991) of new glass handbooks, and a congruence roller. In the case of the ingredient fused during baking, a baking object may be taken out continuously, supplying a raw material during baking. It is desirable to stir melt in the case of the ingredient fused during baking.

[0024] Oxygen content is an ambient atmosphere below 5 volume % preferably, and a baking gas ambient atmosphere is an inert gas ambient atmosphere still more preferably. Nitrogen, an argon, helium, a krypton, a xenon, etc. are mentioned as inert gas. The most desirable inert gas is a pure argon.

[0025] The average grain size of the compound shown by this invention has desirable 0.1-60 micrometers. In order to make it a predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planet ball mill, a revolution air-current mold jet mill, a screen, etc. are used. At the time of grinding, wet grinding which made organic solvents, such as water or a methanol, live together can also be performed if needed. It is desirable to perform a classification, in order to consider as a desired particle size. As the classification approach, there is especially no limitation and it can use a screen, a pneumatic elutriation machine, etc. if needed. A classification can use dry type and wet.

[0026] Although the example of the negative-electrode ingredient of this invention is shown below, this

invention is not limited to these. SnB 0.5P0.5O3 and SnAl 0.3B0.5P0.2O2.7, SnAl 0.3B0.7O2.5 and SnSi 0.8P0.2O3.1, SnSi 0.8B0.2O2.9 and SnSi0.8aluminum 0.2O2.9, SnSi0.6 aluminum 0.2B0.2O2.8 and SnSi0.6 aluminum 0.2P0.2O3, SnSi 0.6B0.2P0.2O3, SnSi0.4 aluminum 0.2B0.4O2.7, SnSi0.6 aluminum 0.1B0.1P0.3O3.25, SnSi0.6 aluminum 0.1B0.3P0.1O3.05, and SnSi0.5 aluminum 0.3B0.4 P0.2 O3.55, SnSi0.5 aluminum 0.3B0.4P0.5O4.30, SnSi0.8 aluminum 0.3B0.2P0.2O3.85, and SnAl0.1 B0.5 P0.5 Mg 0.1F0.2O3.15 [0027] SnSi0.8 Mg 0.2O2.8 and SnSi0.6 aluminum0.2 Mg 0.2O2.7, SnSi0.6 aluminum0.1 B0.2 Mg 0.2O2.85 and SnSi0.8 calcium 0.2O2.8, SnSi0.6 aluminum0.2 calcium 0.2O2.7, SnSi0.6 aluminum0.1 B0.1 P0.1 calcium 0.2O2.95, and SnSi0.5 aluminum0.2 B0.1 P0.1 Mg 0.1O2.8, SnSi0.5 aluminum0.1 B0.2 P0.1 calcium 0.4O3.1, SnSi0.8 Ba 0.2O2.8, SnSi0.6 aluminum0.1 B0.1 P0.1 Ba 0.2O2.95.

[0028] Sn0.9 Mn 0.3B0.4P0.4 calcium0.1 Rb0.1 O2.95 and Sn0.9 Fe0.3 B0.4 P0.4 calcium0.1 Rb 0.1O2.95 and Sn0.8 Pb0.2 calcium0.1 P0.9 O3.35 and Sn0.3 germanium0.7 Ba0.1 P0.9 O3.35 and Sn0.9 Mn0.1 Mg 0.1P0.9O3.35, Sn0.2 Mn0.8 Mg 0.1P0.9O3.35, Sn0.7 Pb0.3 calcium 0.1P0.9O3.35, Sn0.2 germanium0.8 Ba 0.1P0.9O3.35.

[0029] Sn1.6 B0.4 P0.4 calcium 0.2O3.4 and Sn1.3 B0.4 P0.4 calcium 0.2O3.1, Sn1.6 B4 P0.4 Ba 0.2O3.4 and Sn1.3 B0.4 P0.4 Ba 0.2O3.1, Sn1.6 B0.4 P0.4 Mg 0.2O3.4, Sn1.6 aluminum0.1 B0.3 P0.4 calcium 0.2O3.4, [0030] Sn1.3 aluminum 0.1B0.3P0.4K0.2O3, Sn1.0 aluminum 0.1B0.3P0.4K0.2O2.7, Sn1.6 aluminum0.1 B0.3 P0.4 Na 0.2O3.3, Sn1.3 aluminum0.1 B0.3 P0.4 Na 0.2O3, Sn1.0 aluminum0.1 B0.3 P0.4 Na 0.2O2.7, Sn1.6 aluminum0.1 B0.3 P0.4 Rb 0.2O3.3, Sn1.3 aluminum0.1 B0.3 P0.4 Rb 0.2O3, Sn1.0 aluminum0.1 B0.3 P0.4 Rb 0.2O2.7, Sn1.6 aluminum0.1 B0.3P0.4 Cs 0.2O3.3, Sn1.2 aluminum0.1 B0.3P0.4 Cs 0.2O2.9, Sn1.0 aluminum0.1 B0.3 P0.4 Cs 0.2O2.7, Sn1.3 aluminum0.1 B0.3 P0.4 Ba 0.1K0.1O3.05.

[0031] The chemical formula of the compound which baking was carried out [above-mentioned] and obtained is computable from the weight difference of the fine particles before and behind baking as inductively-coupled-plasma (ICP) emission spectrochemical analysis and a brief method as a measuring method.

[0032] 50-700-mol% per negative-electrode ingredient of the amount of light metal insertion to the negative-electrode ingredient of this invention is good until it approximates it to the deposition potential of the light metal, but although it is desirable, it is especially desirable, for example. [100-600-mol% of] Many the burst sizes are so desirable that there are to the amount of insertion. The insertion approach of a light metal has electrochemical and the desirable chemical and thermal approach. The approach of inserting electrochemically the light metal contained in positive active material and the approach of an electrochemical process of inserting in a direct electrochemistry target from a light metal or its alloy are desirable. The chemical approach has mixing with a light metal, contact or an organic metal, for example, butyl lithium etc., and the approach of making it react. An electrochemical process and the chemical approach are desirable. This especially light metal has a lithium or a desirable lithium ion.

[0033] Various elements can be included in the negative-electrode ingredient of this invention. For example, the dopant of a lanthanoids system metal (Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg) and the various compounds (for example, compound of Sb, In, and Nb) which raise electronic conduction nature may also be included. 0-5-mol% of the amount of the compound to add is desirable.

[0034] It can cover with an oxide with a chemical formula which is different from the positive active material used or a negative-electrode ingredient in the front face of the positive active material of the oxide used by this invention, or a negative-electrode ingredient. This scaling object has a desirable oxide containing the compound which dissolves in acidity and alkalinity. A metallic oxide with still higher electronic conduction nature is desirable. for example, PbO2, Fe 2O3, SnO2, In 2O3, ZnO, etc. -- or it is desirable to include dopants (for example, a metal, a halogen, etc. from which a valence differs in an oxide) in these oxides. They are SiO2, SnO2, Fe 2O3, ZnO, and PbO especially preferably. The amount of the metallic oxide used for such surface treatment has 0.1 - 10 desirable % of the weight per this positive active material and negative-electrode ingredient, especially its 0.2 - 5 % of the weight is desirable, and its 0.3 - 3 % of the weight is the most desirable. Moreover, in addition to this, the front

face of positive active material or a negative-electrode ingredient can be reformed. For example, processing by processing, the conductive polymer, polyethylene oxide, etc. by processing and the chelating agent is mentioned by the esterification agent in the front face of a metallic oxide.

[0035] Although the transition-metals oxide which can carry out insertion emission of the lithium ion reversibly is sufficient as the positive active material used by this invention, lithium content transition-metals oxide is especially desirable. As desirable lithium content transition-metals oxide positive active material used by this invention, oxide including the lithium content Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Mo, and W is raised. moreover, alkali metal other than a lithium (the [of the periodic table] the [IA,] element of IIA) -- and -- or aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. may be mixed. 0-30-mol% of the amount of mixing is desirable to transition metals. It is more desirable to mix and compound as desirable lithium content transition-metals oxide positive active material, so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from Ti, V, Cr, Mn, Fe, Co, nickel, Mo, and W with transition metals here) may be set to 0.3-2.2 rather than being used by this invention. It is desirable to mix and compound so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from V, Cr, Mn, Fe, Co, and nickel with transition metals here) may be set to 0.3-2.2 as especially desirable lithium content transition-metals oxide positive active material used by this invention. It is desirable that the especially desirable lithium content transition-metals oxide positive active material used by this invention is Li_xQO_y (Q is mainly the transition metals with which a kind contains Co, Mn, nickel, V, and Fe at least here), $x=0.2-1.2$, and $y=1.4-3$. As Q, aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. may be mixed in addition to transition metals. 0-30-mol% of the amount of mixing is desirable to transition metals.

[0036] As desirable lithium content metallic-oxide positive active material, to the pan used by this invention Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , and $\text{Li}_x\text{Coa nickel1-aO}_2$, $\text{Li}_x\text{Cob V1-b Oz}$ and $\text{Li}_x\text{Cob Fe1-b O}_2$, $\text{Li}_x\text{Mn 2O}_4$, $\text{Li}_x\text{Mnc Co2-c O}_4$, and $\text{Li}_x\text{Mnc nickel2-c O}_4$, $\text{Li}_x\text{Mnc V2-cO}_4$ and $\text{Li}_x\text{Mnc Fe2-c O}_4$, $\text{Li}_x\text{Cob B1-b O}_2$ and $\text{Li}_x\text{Cob Si1-b O}_2$, $\text{Li}_x\text{Mn 2O}_4\text{ MnO}_2$ Mixture and $\text{Li}_2\text{xMnO}_3\text{ MnO}_2$ Mixture, $\text{Li}_x\text{Mn 2O}_4$ and $\text{Li}_2\text{xMnO}_3\text{ MnO}_2$ Mixture (it is $x=0.2-1.2$, $a=0.1$ to 0.9 , $b=0.8$ to 0.98 , $c=1.6-1.96$, and $z=2.01-5$ here) can be raised. As desirable lithium content metallic-oxide positive active material, to the pan used by this invention Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , and $\text{Li}_x\text{Coa nickel1-aO}_2$, $\text{Li}_x\text{Cob V1-b Oz}$ and $\text{Li}_x\text{Cob Fe1-b O}_2$, $\text{Li}_x\text{Mn 2O}_4$, $\text{Li}_x\text{Mnc Co2-c O}_4$, and $\text{Li}_x\text{Mnc nickel2-c O}_4$, $\text{Li}_x\text{Mnc V2-cO}_4$ and $\text{Li}_x\text{Mnc Fe2-c O}_4$ (it is $x=0.7-1.2$, $a=0.1$ to 0.9 , $b=0.8$ to 0.98 , $c=1.6-1.96$, and $z=2.01-2.3$ here) are raised. As most desirable lithium content transition-metals oxide positive active material used by this invention, Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Coa nickel1-a O}_2$, $\text{Li}_x\text{Mn 2O}_4$, and $\text{Li}_x\text{Cob V1-b Oz}$ (it is $x=0.7-1.2$, $a=0.1$ to 0.9 , $b=0.9$ to 0.98 , and $z=2.02-2.3$ here) are raised. Here, the x above-mentioned values are values before charge-and-discharge initiation, and are fluctuated by charge and discharge.

[0037] Although positive active material is compoundable with the approach and solution reaction which mix a lithium compound and a transition-metals compound and are calcinated, especially its calcinating method is desirable. The burning temperature used by this invention has desirable 250-2000 degrees C, and its 350-1500 degrees C are [that what is necessary is just the temperature which some mixed compounds which are used by this invention decompose and fuse] especially desirable. It is desirable to carry out temporary quenching at 250-900 degrees C on the occasion of baking. As firing time, 1 - 72 hours is 2 - 20 hours desirable still more preferably. Moreover, dry type or wet are sufficient as the alligation of a raw material. Moreover, you may anneal at 200 degrees C - 900 degrees C after baking. especially a baking gas ambient atmosphere is limited -- not having -- an oxidizing atmosphere and reducing atmosphere -- all can be taken. For example, the gas which prepared the oxygen density in proportion of arbitration among air or hydrogen, a carbon monoxide, nitrogen, an argon, helium, a krypton, a xenon, a carbon dioxide, etc. are mentioned.

[0038] As an approach of inserting a lithium ion in transition-metals oxide chemically on the occasion of composition of the positive active material of this invention, the approach of compounding by making it react with a lithium metal, a lithium alloy, butyl lithium, and transition-metals oxide is desirable.

Although especially the average grain size of the positive active material used by this invention is not limited, 0.1-50 micrometers is desirable. Although not limited especially as a specific surface area, 0.01-50m²/g is desirable at a BET adsorption method. Moreover, as pH of the supernatant when melting 5g of positive active material to 100ml of distilled water; 12 or less [7 or more] are desirable. In order to make it a predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a vibration ball mill, a vibration mill, a satellite ball mill, a planet ball mill, a revolution air-current mold jet mill, a screen, etc. are used. The positive active material obtained by baking may be used after water, aqueous acids, an alkaline water solution, and an organic solvent wash.

[0039] The combination of the negative-electrode ingredient and positive active material which are used for this invention The compound preferably shown by the general formula (1), and Lix CoO₂ and Lix NiO₂, Lix Co_a nickel_{1-a} O₂, Lix MnO₂, and Lix Mn₂O₄, Or it is the combination of Lix Co_b V_{1-b} O_z. (it is x=0.7-1.2, a= 0.1 to 0.9, b= 0.9 to 0.98, and z=2.02-2.3 here), and the nonaqueous rechargeable battery which excelled [high capacity / high discharge voltage and] in the charge-and-discharge cycle property can be obtained.

[0040] The equivalent of lithium insertion into the negative-electrode ingredient of this invention is 3-10Eq, and determines the amount-used ratio with positive active material according to this equivalent. It is desirable to use for the amount-used ratio based on this equivalent, applying a 0.5 to 2 twice as many multiplier as this. A lithium source of supply determines the amount of the positive active material used according to the lithium emission equivalent of a negative-electrode ingredient (for example, a lithium metal, an alloy, butyl lithium, etc.) except positive active material. It is desirable to use for the amount-used ratio based on this equivalent also at this time, also applying a 0.5 to 2 twice as many multiplier as this.

[0041] It is desirable to use the foil and metal powder of a lithium metal and a lithium alloy (alloy of aluminum, aluminum-Mn, aluminum-Mg, aluminum-Sn, aluminum-In, aluminum-Cd, and a lithium) as a lithium source of supply beforehand, when inserting the lithium in the negative electrode from lithium sources of supply other than a positive electrode. these metallic foils etc. -- a negative electrode -- you may make it located through the protective layer of direct or this invention on a mixture moreover, a negative electrode -- you may make it located on a charge collector without a mixture A foil may give an about 20-micrometer thin thing to homogeneity, and may arrange a thicker thing partially. The thickness of a foil can be decided to be the nature after cell formation from the amount inserted in a negative electrode.

[0042] an electrode -- an electric conduction agent, a binder, a filler, etc. can be added to a mixture. In the constituted cell, if an electric conduction agent is an electronic conduction nature ingredient which does not cause a chemical change, it is good anything. Usually, conductive ingredients, such as natural graphites (flaky graphite, a scale-like graphite, earthy graphite, etc.), an artificial graphite, carbon black, acetylene black, KETCHIEN black, carbon fiber metallurgy group powder (copper, nickel, aluminum, silver, etc.), a metal fiber, or a polyphenylene derivative, can be included as one sort or such mixture. Especially concomitant use of a graphite and acetylene black is desirable. The addition has 1 - 50 desirable % of the weight, and its 2 - 30 % of the weight is especially desirable. In carbon or especially a graphite, 2 - 15 % of the weight is desirable.

[0043] In a binder, usually Starch, polyvinyl alcohol, a carboxymethyl cellulose, Hydroxypropylcellulose, a regenerated cellulose, diacetyl cellulose, Polyvinyl chloride, a polyvinyl pyrrolidone, tetrafluoroethylene, Polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), The polymer which has polysaccharide, such as sulfonation EPDM, styrene butadiene rubber, polybutadiene, a fluororubber, and polyethylene oxide, thermoplastics, and rubber elasticity is used as one sort or such mixture. Moreover, when using like polysaccharide a lithium and the compound containing a functional group which reacts, it is desirable to add a compound like an isocyanate radical and to carry out deactivation of the functional group. The addition of the binder has 1 - 50 desirable % of the weight, and its 2 - 30 % of the weight is especially desirable. In the constituted cell, a filler can be used anything, if it is the fibrous ingredient which does

not cause a chemical change. Usually, fiber, such as olefin system polymers, such as polypropylene and polyethylene, glass, and carbon, is used. Although especially the addition of a filler is not limited, 0 - 30 % of the weight is desirable.

[0044] the moisture powder which contains the compound of this invention in using the negative-electrode ingredient of this invention in a nonaqueous rechargeable battery system -- a mixture -- a paste -- a charge collector top -- spreading and desiccation -- carrying out -- and this moisture powder -- a mixture -- it is desirable that pH of a paste is less than [5 or more] 10 and less than [further 6 or more] 9. Moreover, it is desirable to keep the temperature of this moisture powder paste at 5 degrees C or more less than 80 degrees C, and to perform spreading of a up to [a charge collector] within seven days after preparation of a paste.

[0045] As a separator, it has big ion transmittance, and has a predetermined mechanical strength, and an ingredient with insulating fine porosity or a clearance is used. Furthermore, for the improvement in safety, it is required to have the function which blockades the above-mentioned clearance above 80 degrees C, raises resistance, and intercepts a current. 90 degrees C or more 180 degrees C or less of lock out temperature of these clearances are 110 degrees C or more 170 degrees C or less more preferably. How to make a clearance may be which a well-known approach, although it changes with ingredients. In the case of a porosity film, the configurations of a hole are usually a round shape and an ellipse form, magnitude is 0.05 micrometers to 30 micrometers, and 0.1 to its 20 micrometers are desirable. Furthermore, you may be the hole of the shape of a rod, or an indeterminate form like [at the time of making by the extending method and the phase separation method]. In the case of cloth, a clearance is an opening between fiber and it is dependent on how to make textile fabrics and a nonwoven fabric. It is 20% to 90%, the ratio, i.e., the porosity, to which these clearances close, and it is desirable. [35 to 80% of]

[0046] 5 micrometers or more 100 micrometers or less of separators of this invention are cloth, such as a film [80 micrometers or less] 10 micrometers or more of fine porosity, textile fabrics, and a nonwoven fabric, more preferably. The thing with that desirable especially desirable in which the separator of this invention contains an ethylene component at least 20% of the weight is included 30% or more. As components other than ethylene, a propylene, a butene, a hexene, fluoride ethylene, a vinyl chloride, vinyl acetate, and acetalization vinyl alcohol are raised, and a propylene and especially fluoride ethylene are desirable. As for the film of fine porosity, what consists of polyethylene, an ethylene propylene copolymerization polymer, or an ethylene butene copolymerization polymer is desirable. Furthermore, what carried out the mixed dissolution and made polyethylene, polypropylene and polyethylene, and Pori ethylene tetrafluoride is desirable. As for a nonwoven fabric or textile fabrics, what the path of yarn is 0.1 micrometers to 5 micrometers, and becomes from polyethylene, an ethylene propylene copolymerization polymer, an ethylene butene-1 copolymerization polymer, an ethylene methylbutene copolymerization polymer, an ethylene methyl pentene copolymerization polymer, polypropylene, and Pori ethylene tetrafluoride fiber yarn is desirable. These separators may be single ingredients or may be composite material. Especially the thing that compounded the ingredient of a gestalt with which the thing and microporous film which carried out the laminating of two or more sorts of microporous film into which an aperture, porosity, the lock out temperature of a hole, etc. were changed especially, a nonwoven fabric and microporous film, and textile fabrics and a nonwoven fabric differ from paper etc. is desirable. The separator of this invention may contain the particle of inorganic substances, such as inorganic fibers, such as a glass fiber and a carbon fiber, a silicon dioxide, a zeolite and an alumina, and talc. Furthermore, what processed and carried out hydrophilization of an opening or the front face with the surfactant may be used.

[0047] As an electrolyte, as an organic solvent, propylene carbonate, ethylene carbonate, Butylene carbonate, dimethyl carbonate, diethyl carbonate, Gamma-butyrolactone, 1, 2-dimethoxyethane, a tetrahydrofuran, 2-methyl tetrahydrofuran, dimethyl sulfoxide, 1, 3-dioxolane, A formamide, dimethylformamide, dioxolane, an acetonitrile, Nitromethane, methyl formate, methyl acetate, methyl propionate, ethyl propionate, Trialkyl phosphate, trimethoxy methane, a dioxolane derivative, a sulfolane, 3-methyl-2-oxazolidinone, a propylene carbonate derivative, The lithium salt which melts into

the solvent which mixed at least one or more sorts of aprotic organic solvents, such as tetrahydrofuran derivative, diethylether, 1, and 3-propane aprotic, and its solvent, For example, LiClO_4 , LiBF_4 , LiPF_6 , and LiCF_3SO_3 , It consists of one or more sorts of salts, such as LiCF_3CO_2 , LiAsF_6 , LiSbF_6 , $\text{LiB}10\text{Cl}10$, a low-grade aliphatic-carboxylic-acid lithium, LiAlCl_4 , LiCl , LiBr , LiI , a chloro borane lithium, and 4 phenyl lithium borate. Especially, they are LiCF_3SO_3 , LiClO_4 , and LiBF_4 to the mixed liquor of propylene carbonate or ethylene Cabot, 1 and 2-dimethoxyethane and/, or diethyl carbonate. And/or LiPF_6 The included electrolytic solution is desirable. It is LiBF_4 to the mixed liquor of ethylene Cabot and diethyl carbonate. And/or LiPF_6 Especially the included electrolytic solution is desirable. although especially the amount that adds these electrolytes in a cell is not limited -- positive active material, the amount of a negative-electrode ingredient, and the size of a cell -- **** for initial complements -- things are made. The concentration of a supporting electrolyte has desirable 0.2-3 mols per 1l. of electrolytic solutions.

[0048] Moreover, the following solid electrolytes can also be used besides the electrolytic solution. It is divided into an inorganic solid electrolyte and an organic solid electrolyte as a solid electrolyte. The nitride of Li, the halogenide, the oxygen acid salt, etc. are well known by the inorganic solid electrolyte. Especially, Li_3N , LiI , Li_5NI_2 , $\text{Li}_3\text{N-LiI-LiOH}$, LiSiO_4 , $\text{LiSiO}_4\text{-LiI-LiOH}$, $x\text{Li}_3\text{PO}_4\text{-(1-x) Li}_4\text{SiO}_4$, Li_2SiS_3 , a phosphorus sulfide compound, etc. are effective. The mixture of the polymer which contains a polyethylene oxide derivative or this derivative in an organic solid electrolyte, the polymer containing a polypropylene oxide derivative or this derivative, the polymer containing an ionic dissociation radical, the polymer containing an ionic dissociation radical, and the above-mentioned aprotic electrolytic solution, and phosphoric ester polymer - are effective. Furthermore, there is also the approach of adding a polyacrylonitrile to the electrolytic solution. Moreover, how to use inorganic and an organic solid electrolyte together is also learned.

[0049] As a separator, it has big ion transmittance, and has a predetermined mechanical strength, and an insulating thin film is used. The sheet and nonwoven fabric which were built from organic solvent-proof nature and hydrophobicity from an olefin system polymer, a glass fiber, or polyethylene, such as the poly pre pyrene, etc. are used. The range where the aperture of a separator is generally used as an object for cells is used. For example, 0.01-10 micrometers is used. Generally the thickness of SEPARATA is used in the range for cells. For example, 5-300 micrometers is used. Moreover, adding to an electrolyte the compound shown below in order to improve discharge and a charge-and-discharge property is known. For example, a pyridine, a triethyl FOSU fight, triethanolamine, Cyclic ether, ethylenediamine, n-glyme, hexalin acid TORIAMIDO, A nitrobenzene derivative, sulfur, a quinonimine dye, N-permutation oxazolidinone, and N and N'-permutation imidazolidinone, Ethylene glycol dialkyl ether, quarternary ammonium salt, a polyethylene glycol, A pyrrole, a 2-methoxyethanol, AlCl_3 , the monomer of a conductive polymer electrode active material, The triethylenephosphoramidate, trialkylphosphine, morpholine, An aryl compound and hexamethylphosphoric triamide with a carbonyl group, 4-alkyl morpholine and the bicyclic third class amine, oil (JP,62-287,580,A), the fourth class phosphonium salt, the third class sulfonium salt, etc. are mentioned.

[0050] Moreover, in order to make the electrolytic solution into incombustibility, a halogen-containing solvent, for example, a carbon tetrachloride, and a 3 fluoridation ethylene chloride can be included in the electrolytic solution. Moreover, in order to give fitness to elevated-temperature preservation, carbon dioxide gas can be included in the electrolytic solution. Moreover, the electrolytic solution or an electrolyte can be included in the mixture of a positive electrode or a negative electrode. For example, the approach of including said ion conductive polymer and nitromethane, and the electrolytic solution is learned.

[0051] If it is the electronic conductor which does not cause a chemical change in the constituted cell as a charge collector of a forward negative electrode, it is good anything. For example, the thing which made carbon, nickel, titanium, or silver process on the front face of aluminum or stainless steel else [, such as stainless steel, nickel, aluminum, titanium, and carbon] is used as an ingredient at a positive electrode. Especially, aluminum or an aluminium alloy is desirable. The thing which made the negative electrode process carbon, nickel, titanium, or silver as an ingredient on the front face of copper or

stainless steel else [, such as stainless steel, nickel, copper, titanium aluminum, and carbon], an aluminum-Cd alloy, etc. are used. Especially, copper or a copper alloy is desirable. Oxidizing the front face of these ingredients is also used. Moreover, it is desirable to attach irregularity to a current collection body surface by surface treatment. As for a configuration, a film besides the foil, a sheet, the thing netted and punched, a lath object, a porous body, foam, the Plastic solid of a fiber group, etc. are used. Although especially thickness is not limited, a 1-500-micrometer thing is used.

[0052] The configuration of a cell can apply coin, a carbon button, a sheet, a cylinder, flatness, an angle, etc. to all. The configuration of a cell is compressed into the configuration of a pellet at the time of coin or a carbon button, and the mixture of positive active material or a negative-electrode ingredient is mainly used. The thickness and the diameter of the pellet are decided with the magnitude of a cell. Moreover, when the configurations of a cell are a sheet, a cylinder, and an angle, on a charge collector, the mixture of positive active material or a negative-electrode ingredient is applied, (coat) dried and compressed, and is mainly used. A general approach can be used for the method of application. For example, the reverse roll method, the direct rolling method, the blade method, the knife method, the extrusion method, the curtain method, the gravure method, the bar method, a dip method, and the squeeze method can be mentioned. The blade method, the knife method, and the extrusion method are desirable also in it. As for spreading, it is desirable to carry out the rate for 0.1-100m/. Under the present circumstances, according to the solution physical properties of a mixture, and drying, the surface state of a good spreading layer can be acquired by selecting the above-mentioned method of application. The time of one side [every] ** or double-sided coincidence is sufficient as spreading. Moreover, continuation, an intermission, or a stripe is sufficient as spreading. Although the thickness, die length, and width of the spreading layer are decided with the magnitude of a cell, the thickness of the spreading layer of one side is in the condition of having been compressed after dry, and especially its 1-2000 micrometers are desirable.

[0053] The approach generally adopted can be used as a pellet, or desiccation of a sheet or the dehydration approach. Especially, it is desirable independent or to combine and to use hot blast, a vacuum, infrared radiation, far infrared rays, an electron ray, and a damp wind. The range of temperature of 80-350 degrees C is desirable, and it is especially desirable. [of the range which is 100-250 degrees C] moisture content -- the cell whole -- 2000 ppm or less -- desirable -- a positive electrode -- a mixture and a negative electrode -- it is desirable to make it 500 ppm or less in a mixture or an electrolyte, respectively in respect of cycle nature. Although the approach generally adopted can be used for a pellet or the method of pressing a sheet, a die-press method and its calender pressing method are especially desirable. Especially press ** is 0.2 - 3 t/cm², although not limited. It is desirable. The pressing speed of the calender pressing method has the amount of desirable 0.1-50m/, and press temperature has desirable room temperature -200 degree C. As for the ratio of negative-electrode sheet width of face to a positive-electrode sheet, 0.9-1.1 are desirable, and 0.95-especially 1.0 are desirable. the content ratio of positive active material and a negative-electrode ingredient -- a compound class and a mixture -- although it cannot limit since it changes with formulas, it can be set as the optimal value in the viewpoint of capacity, cycle nature, and safety.

[0054] this -- a mixture -- after rolling or folding those sheets after piling up through a sheet and a separator, inserting them in a can and connecting a sheet with a can electrically, they pour in the electrolytic solution and form a cell can using an obturation plate. At this time, a relief valve can be used as an obturation plate. It may be equipped with the various insurance components known from the former besides a relief valve. For example, a fuse, bimetal, a PTC component, etc. are used as an overcurrent-protection component. Moreover, the approach of making a cut in a cell can, the gasket crack approach, the obturation plate crack approach, or cutting process with a lead plate can be used for everything but a relief valve as a cure of an internal pressure rise of a cell can. Moreover, the protection network which built overcharge and the cure against overdischarge into the battery charger may be made to provide, or you may make it connect independently. Moreover, the method which intercepts a current by the rise of cell internal pressure can be provided as a cure against overcharge. At this time, the compound which raises internal pressure can be included in a mixture or an electrolyte. as the example

of the compound used in order to raise internal pressure -- Li_2CO_3 , LiHCO_3 , Na_2CO_3 , NaHCO_3 , CaCO_3 , and MgCO_3 etc. -- a carbonate etc. can be mentioned.

[0055] A metal and an alloy with electrical conductivity can be used for a can or a lead plate. For example, metals or those alloys, such as iron, nickel, titanium, chromium, molybdenum, copper, and aluminum, are used. A well-known approach (electric welding of an example, a direct current, or an alternating current, laser welding, ultrasonic welding) can be used for the welding process of a cap, a can, a sheet, and a lead plate. The compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation.

[0056] Although not limited to especially the application of the nonaqueous rechargeable battery of this invention, when it carries in electronic equipment, for example, A color notebook computer, monochrome notebook computer, a pen input personal computer, a pocket (palm top) personal computer, A note type word processor, a pocket word processor, an Electronic Book player, a cellular phone, Carrying facsimile a cordless phon -- a cordless handset, a pager, and a handy terminal -- A pocket copy, a pocket printer, a headphone stereo, a video movie, A liquid crystal television, a handy cleaner, portable CD, a mini disc, an electric shaver, an electronic translating machine, a land mobile radiotelephone, a transceiver, a power tool, an electronic notebook, a calculator, memory card, a tape recorder, radio, a backup power supply, memory card, etc. are mentioned. In addition, as a noncommercial use, an automobile, an electric car, a motor, a luminaire, a toy, a game device, a load conditioner, an iron, a clock, a stroboscope, a camera, medical equipment (a pace maker, hearing aid, and a shoulder are also **** etc.), etc. are mentioned. Furthermore, it can use as the various objects for munitions, and an object for space. Moreover, it is also combinable with a solar battery.

[0057]

[Example] Although an example is raised to below and this invention is explained in more detail, unless the main point of invention is exceeded, this invention is not limited to an example.

[0058] 13.5g of synthetic example -1 tin protoxides, 3.6g of silicon dioxides, 0.64g of magnesium oxides, and 0.69g of oxidation boron were blended dryly, it put into the crucible made from an alumina, and the temperature up was carried out to 1000 degrees C by part for bottom 15-degree-C/of argon atmosphere. After calcinating at 1200 degrees C for 10 hours, the temperature was lowered even to the room temperature by part for 10-degree-C/, it took out from the firing furnace, coarse grinding of this was carried out, the jet mill ground further, and $\text{SnSi}_0.6\text{Mg}_0.2\text{B}_0.2\text{O}_2.7$ (compound 1-A) with a mean particle diameter of 4.5 micrometers was obtained. Moreover, it is the object which has the broadcloth peak which has top-most vertices near 28 degree with 2theta value in the X-ray diffraction method using CuK alpha rays, and the crystalline diffraction line was not looked at by 40 degrees or more 70 degrees or less with 2theta value.

[0059] By the same approach, the raw material of the amount of stoichiometries was mixed, calcinated and ground, respectively, and the following compound was obtained. $\text{SnSi}_0.8\text{Mg}_0.2\text{O}_2.8$ (1-B), $\text{SnSi}_0.6\text{aluminum}_0.2\text{Mg}_0.2\text{O}_2.7$ (1-C), $\text{SnSi}_0.6\text{P}_0.2\text{Mg}_0.2\text{O}_2.9$ (1-D), $\text{SnSi}_0.6\text{aluminum}_0.1\text{B}_0.2\text{Mg}_0.1\text{O}_2.75$ (1-E), and $\text{SnSi}_0.5\text{P}_0.1\text{B}_0.1\text{Mg}_0.3\text{O}_2.7$ (1-F).

[0060] As an example-1 negative-electrode ingredient, using compound 1-A compounded in the synthetic example -1, it was mixed at a rate of 6 % of the weight of scale-like graphites 88% of the weight, further, 1 % of the weight of carboxymethyl-celluloses and 1 % of the weight of acetic-acid lithiums were added for the water distribution object of Pori fluoride kinky thread NIDEN 4% of the weight, water was kneaded as a medium as a binder, and the slurry was produced. This slurry was applied to both sides of copper foil with a thickness of 18 micrometers by the extrusion method, and the negative electrode a was made. On the negative electrode a, alpha-aluminum-2 O3-97 (1-micrometer of mean-diameters)% of the weight, it mixed at a rate of 3 % of the weight of carboxymethyl-celluloses, and the negative-electrode b applied and created that which kneaded water as a medium and slurred it. these negative electrodes, and a and b -- the calender press machine after desiccation -- compression molding -- carrying out -- predetermined width of face and die length -- cutting -- band-like each -- a negative-electrode sheet, and a and b were produced. The negative-electrode sheet a was [78 micrometers and the negative-electrode sheet b of the thickness of a negative-electrode sheet] 100

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micrometers. As a positive-electrode ingredient, it is LiCoO_2 . 87% of the weight, 6 % of the weight of scale-like graphites, and 3 % of the weight of acetylene black, 3 % of the weight of polytetrafluoroethylene water distribution objects and 1 % of the weight of sodium polyacrylate were further added as a binder, the slurry which kneaded water as a medium and was obtained was applied to both sides of aluminium foil with a thickness of 20 micrometers by the same approach as the above, and the positive electrode a was made. On the positive electrode a, alpha-aluminum 2 O3 97 (1 micrometer of mean diameters)% of the weight, it mixed at a rate of 3 % of the weight of carboxymethyl celluloses, and the positive electrode b applied and created that which kneaded water as a medium and slurred it. These positive electrodes, and a and b were dried, pressed and cut, and a positive-electrode sheet, and a and b were made. The positive-electrode sheet a was [250 micrometers and the positive-electrode sheet b of the thickness of a positive-electrode sheet] 265 micrometers. The negative-electrode sheet a, the positive-electrode sheet a, the negative-electrode sheet b, and the positive-electrode sheet b were combined, and Cell A (for a comparison) and Cell B (this invention) were made by the approach described below. A negative-electrode sheet and a positive-electrode sheet are each the dew-point after carrying out spot welding of the lead plate of nickel and aluminum to an edge, respectively. - Dehydration desiccation was carried out in dry air 40 degrees C or less for 150-degree-C 2 hours. Furthermore, the laminating was carried out in the order of a dried [dehydration] positive-electrode sheet (8), fine porosity polypropylene film separator (Celgard 2400), a dried [dehydration] negative-electrode sheet (9), and a separator (10), this was involved in, and it wound around the curled form by the opportunity.

[0061] It contained with the iron closed-end cylindrical cell can (11) which serves this winding object as a negative-electrode terminal and which performed nickel plating. 1L per LiPF_6 LiBF_4 Respectively, 0.05 mols were contained and 0.95 and the electrolyte with which a solvent consists of ethylene carbonate and diethyl carbonate 2:8 capacity mixed liquor were poured into the cell can. the cell lid (12) which has a positive-electrode terminal -- a gasket (13) -- minding -- the cylindrical cell was produced in total. In addition, the positive-electrode terminal (12) connected beforehand the positive-electrode sheet (8) and the cell can (11) with the negative-electrode sheet (9) with the lead terminal. The cross section of a cylindrical cell was shown in drawing 1. In addition, (14) is a relief valve. It creates ten pieces at a time, respectively, and Cell A (for a comparison) and Cell B (this invention) are 1 mA/cm². After charging to 4.15V, it saved for three weeks at 60 degrees C. The open circuit voltage of each cell was measured after three weeks, and the following result was obtained.

Cell number Cell A (comparison cell) Cell B (cell of this invention)

***** 1 0.92 4.12 2 1.02 4.10 3 1.00 4.08 4 0.78 4.09 5 0.98 4.11 6 1.12 4.13 7 1.03 4.11 80.91 4.089 0.81 4.0910 0.54 The cell of this invention has few voltage drops under preservation clearly, and the result of 4.11 or more shows that the engine performance is stable.

[0062] It produced the 300 same cells as the cells A and B of example-2 example 1 at a time, respectively, and charged to 4.15V. When asked for the number of the cell of poor charge, by the cell A for a comparison, by the cell B of six pieces and this invention, it is zero piece and it turned out that the defective incidence rate is improved clearly.

[0063] When 1-B to 1-F was used and the same experiment as example-1 was conducted instead of negative-electrode ingredient 1-A used by example-3 example-1, the almost same result as example-1 was obtained.

Cell C was made combining the negative-electrode sheet b of example-4 example-1, and the positive-electrode sheet a. Cell D was made combining the positive-electrode sheet c and the negative-electrode sheet a which changed the thickness of a protective layer and were made into 280 micrometers of sheet thickness instead of. [the positive-electrode sheet b] When the same experiment as example-1 was conducted using these cells C and D, it turned out that the voltage drop after saving at the cell B said appearance is the stability of the engine performance few. However, open circuit voltage was falling more slightly [C and D] than Cell B.

On the negative electrode a of example -5 example -1, alpha-aluminum 2O3 94 (1 micrometer of mean diameters)% of the weight, it mixed at a rate of 3 % of the weight of scale-like graphites, and 3 % of the

weight of carboxymethyl celluloses, and what applied and produced that which kneaded water as a medium and slurred it was used as the negative electrode c. Cell B and the cell produced similarly were set to E, respectively except using c for a negative-electrode sheet. When the same experiment as an example -1 was conducted using Cell E, the almost same result as an example -1 was obtained. On the negative electrode a of example -6 example -1, alpha-aluminum 2O3 94.5 (1 micrometer of mean diameters)% of the weight, it mixed at 4.5 % of the weight of polyvinylidene fluorides, and a rate of 1 % of the weight of carboxymethyl celluloses, and what applied and produced that which kneaded water as a medium and slurred it was used as the negative electrode d. Cell B and the cell produced similarly were set to F except using d for a negative-electrode sheet. When it produces ten Cells B, the cells E of an example -5, and Cells F of an example -1 at a time, respectively and charges by 4.15-2.8V, it is 5 mA/cm². Discharge capacity and 1 mA/cm² Discharge capacity was measured and the following result was obtained. The rate when making capacity of Cell B into 100% showed the discharge capacity of front Naka.

5 mA/cm² Discharge capacity / 1 mA/cm² Discharge capacity Cell B Cell E Cell F 1 88 89 81 2 87 89 82 3 90 89 82 4 88 90 82 5 89 89 81 6 88 90 82 7 88 88 80 8 89 88 82 9 88 89 82 10 88 89 82 1 mA/cm² Discharge capacity average 100 101 From the result or more of 89, capacity is clearly large and the cell of this invention is 5 mA/cm². Discharge capacity / 1 mA/cm² It turns out that it excels in discharge capacity.

On the negative electrode a of example -7 example -1, alpha-aluminum 2O3 93 (1 micrometer of mean diameters)% of the weight, it mixed at 3 % of the weight of scale-like graphites, 3 % of the weight of polyvinylidene fluorides, and a rate of 1 % of the weight of carboxymethyl celluloses, and what applied and produced that which kneaded water as a medium and slurred it was used as the negative electrode d. Moreover, only coverage was reduced by the same approach as the positive electrode a of an example -1, it considered as the positive electrode with a thickness of 225 micrometers, and what attached the same protective layer as a positive electrode b to this was used as the positive electrode d. On the negative-electrode sheet c of an example -5, and the negative-electrode sheet d, the 120mg [per 1g of negative-electrode ingredients] lithium metal was made into the shape of a strip of paper, and was stuck, and Cell B and the cell produced similarly were used as Cells G and H, respectively except combining the positive-electrode sheet d. It produced ten of these at a time, respectively, the same trial as an example -6 was performed, and the following result was obtained. The rate when making capacity of Cell G into 100% showed the discharge capacity of front Naka.

5 mA/cm ² の放電容量 / 1 mA/cm ² の放電容量			
	電池G	電池H	
1	88	80	
2	89	81	
3	88	80	
4	88	79	
5	89	77	
6	89	78	
7	88	78	
8	88	80	
9	90	79	
10	89	80	
1 mA/cm ² の放電容量平均	100	75	

From the above result, capacity is clearly large and the cell of this invention is 5 mA/cm². Discharge capacity / 1 mA/cm² It turns out that it excels in discharge capacity.

[0064]

[Effect of the Invention] Like this invention, a nonaqueous rechargeable battery with preservation

stability can be made from high discharge operating potential and a big discharge capacity to stability by giving at least one layer of protective layers which become a negative electrode and/or a positive electrode from a solid particulate and a water-soluble polymer in the positive electrode which contains reversibly the ingredient in which occlusion emission is possible for a lithium and a negative electrode, the nonaqueous electrolyte containing lithium salt, and the nonaqueous rechargeable battery that consists of a separator.

[Translation done.]